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Conditioning Effects on Thermal and Dynamic Mechanical Properties of Injection Moulded Glass Fibre Reinforced Polyamide 6,6 Composites

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ABSTRACT

Polymer composites of polyamide 6,6 reinforced with short glass fiber were prepared by injection molding, conditioned under dry, 50% relative humidity (RH) and wet. Molded specimens were analyzed by thermogravimetric analyzer (TGA), differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). TGA results revealed that glass fiber loading in PA 6,6 improve the thermal stability of the composites by an increase in T_{onset} and $T_{50\%}$ as well as DT_p values. DSC analysis revealed that the incorporation of glass fiber and moisture into the PA 6,6 matrix resulted in a remarkable decrease in the degree of crystallinity. However, the melting and crystallization temperatures of the composites are not significantly altered. DMA results revealed the glass transition temperatures are sensitive to moisture absorption and their values move to a lower temperature upon exposure to moisture.

Keywords

Conditioning effects, injection molding, glass fiber composites, thermal properties, dynamic mechanical properties

1. INTRODUCTION

Thermoplastics such as poly(butylenes terephtalate), polypropylene and polyamides are excellent for use in composite materials for their performance-processability-profitability ratios. Properties of thermoplastic composites arise from the combination of fiber and matrix properties and the ability to transfer stresses across the fiber/matrix interphases [1]. The effects of constant moisture content on the mechanical properties of polymers have been widely studied and are fairly well understood In general, moisture diffusion in a composite depends on factors such as volume fraction of fiber, voids, viscosity of matrix, humidity and temperature [2].

The objective of this work is to investigate the influence of glass as reinforcement in composites and the effect of conditioning (dry, 50% R.H. and wet) on thermal and dynamic mechanical of the injection molded glass fiber reinforced polyamide 6,6 composites.

2. EXPERIMENTAL

2.1 Materials, Specimen Preparation and Conditioning

Materials used for the characterization were Technyl® A216 (unreinforced polyamide 6,6) and Technyl® A216 V30 NAT (short glass fiber reinforced polyamide 6,6 composites, 16% fiber volume fraction, V_f). Composites with three different fiber volume fractions, V_f of 4%, 8% and 12% were prepared by diluting of Technyl® A216 V30 NAT with Technyl® A216.

For the specimen preparation, a single gated double cavity, impact and tensile standard test bar mould was used in the molding, using Boy® 50 tonne clamping force injection molding machine. The dimensions of dumb-bell shaped tensile test pieces were in accordance with the ASTM Standard D638 [3].

For dry specimens, they were kept in vacuumed desiccators with silica gel immediately after the molding. For 50% R.H. condition, the specimens were exposed to saturated sodium hydrogen sulphate ($NaHSO_4$) solution environment in the desiccators for at least a month [4]. For wet conditioning, the samples were immersed in boiling water for at least 24 hours.

2.2 Determination of Thermal and Dynamic Mechanical Properties

Thermogravimetric analysis (TGA) was investigated by using the TGA 6 Thermogravimetric Analyzer (Perkin Elmer) to study the thermal decomposition behavior of composites. Tests were done under nitrogen at a scan rate of 10°C/min in a programmed temperature range of 50°C to 900°C. A test sample of 5-10 mg was used for the run. Differential scanning calorimetry (DSC) experiments were performed with a Diamond DSC (Perkin Elmer). Each sample was subjected to heating and cooling treatment at a scanning rate of 10°C/min under nitrogen atmosphere so as to prevent oxidation. A test sample of 5-10 mg was placed in an aluminum pan and tested over a temperature range of 0°C to 290°C.

The dynamic mechanical properties of specimens were analyzed with a Dynamic Mechanical Analyzer, DMA Q800 (Thermal Analysis Instrument). Test specimens were taken from the middle section of the injection molded dumb-bell test bar and were subjected to three-point bending mode with a support span of 50 mm. Measurements were conducted over a temperature range of –100°C to 150°C with a heating rate of 3°C/min under a constant frequency of 1.0 Hz.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric Analysis (TGA)

Figures 1 and 2 show the TGA curves for all composites in the range of study under dry and wet conditions respectively. The thermal stability is characterized by the onset, derivative peak temperature and the temperatures at 50% of weight loss, which are referred as T_{onset}, DT_P and $T_{50\%,}$ respectively, as tabulated in Table 1.

Table 1: TGA thermogravimetric data of glass fiber composites under dry and wet conditions.

Sample	Decomposition Temperature (°C)	$T_{50\%}$ (°C)	T_{onset} (°C)	DT_P (°C)
V_f 0% Dry	332 – 797	472	445	478
V_f 0% Wet	301 – 799	426	416	426
V_f 4% Dry	330 – 704	474	447	477
V_f 4% Wet	303 – 705	477	447	478
V_f 8% Dry	331 – 706	482	447	487
V_f 8% Wet	302 – 685	480	445	479

Gradual weight loss in the temperature range of 301°C to 799°C indicates the matrix content of the composites. The temperature range of 50°C to 200°C corresponds to the gradual weight loss due to evaporation of moisture. For wet samples, the percentage weight loss of 6% to 7% reflects the maximum moisture absorption by the samples. However, in dry samples, there is no existence of moisture in this temperature range, indicating no trap water/moisture by the polymer matrix. The decomposition of PA 6,6 matrix starts at a temperature of 332°C and reaches nearly 100% at 797°C.

It is a common practice to consider 50% weight loss as an indicator for structural destabilization [5]. For composites under dry condition, the temperature at 50% weight loss, $T_{50\%}$ for composites at both fiber loadings occur at about 2°C and 10°C higher than that of neat PA 6,6. For composites under wet condition, the $T_{50\%}$ were shifted by 51°C and 54°C for composites with fiber V_f of 4% and 8% respectively, compared to the pure matrix. Even though PA 6,6 matrix under wet condition shows a thermal stability remarkably lower than the matrix under dry condition, the TGA curves of PA 6,6 composites, for both 4% and 8% V_f glass fiber indicate a marked increase in thermal stability with respect to the wet matrix. These results suggest that the incorporation of glass fiber into the system has improved the structural destabilization point of the composites.

According to the above results, the glass fiber loading in PA 6,6 produced positive effects on the thermal stability of the composites. The increment of DT_P values of the composites under both conditions compared to neat PA 6,6 (Table 1) also confirms the good thermal stability of these materials [6].

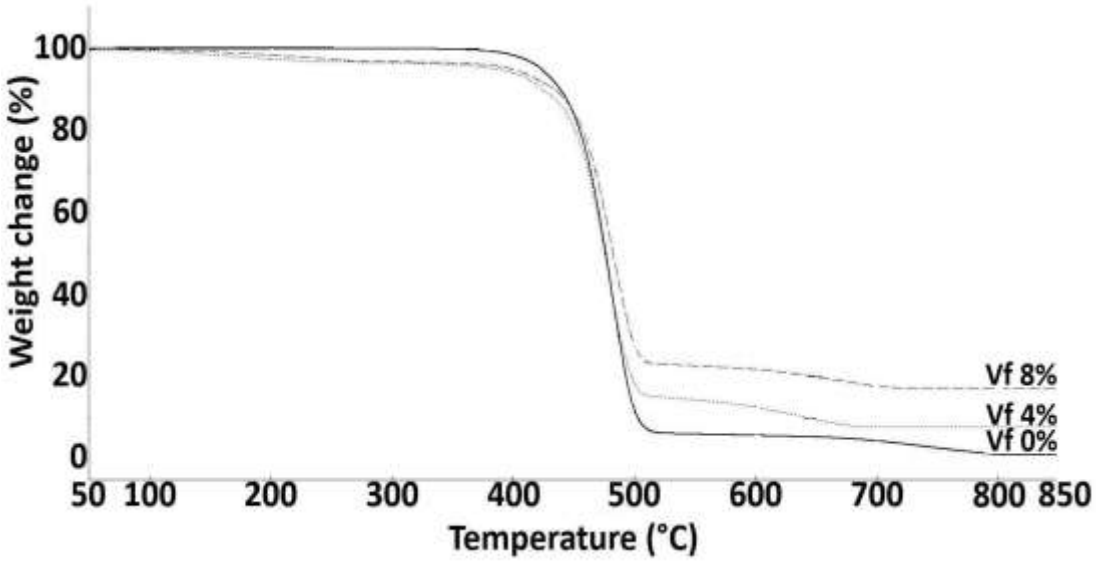

Figure 1: TGA thermographs of injection-molded short glass fiber composites under dry condition

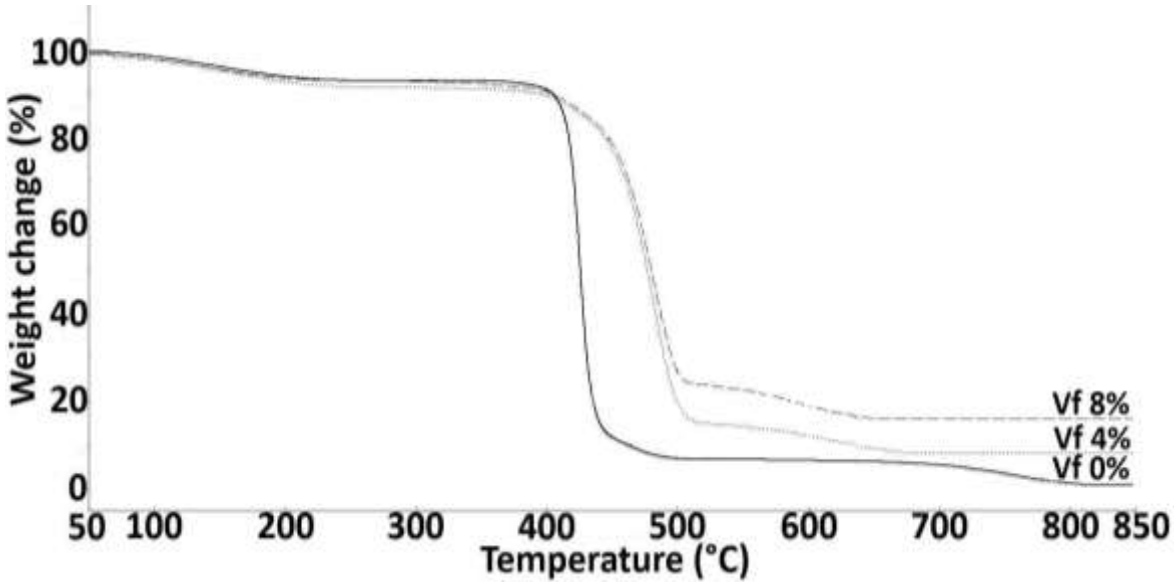

Figure 2: TGA thermographs of injection-molded short glass fiber composites under wet condition

3.2 Differential Scanning Calorimetry (DSC)

The DSC thermograms of injection-molded short glass fiber composites under dry and wet conditions are given in Figures 3 and 4 respectively. The DSC thermograms allow one to estimate the melting temperature (T_m), crystallization temperature (T_c), also degree of crystallinity (X_c) of the composites after the melt-crystallization process by using a reference heat of fusion [7]. In this work, the reference value for the purely crystalline PA 6,6 is taken as 197 J/g (ΔH_m^*). The degree of crystallinity (X_c) is calculated by using the following equation:

$$X_c = \frac{\Delta H_m}{\Delta H_m^*} \times 100 \ (\%)$$

where ΔH_m and ΔH_m^* are the enthalpies of composite specimen and purely crystalline PA 6,6 matrix respectively. Incorporation of glass fibers into the PA 6,6 matrix results in a remarkable decrease in X_c value than pure PA 6,6. The X_c of the composites under dry condition decreases from 37.5% for PA 6,6 matrix to 31.7% and 30.9% for 4% and 8% V_f glass fiber

composites respectively. This suggests that there is a significant change in the microstructure of the PA 6,6 matrix as a result of the incorporation of glass fibers [8]. The same behavior is observed for composites under wet condition.

In terms of conditioning, the incorporation of water into the system also reduces the degree of crystallinity. This is expected as the hydrogen bonds between the molecules are weakened. However, the existence of moisture is not the primary determining factor for polymer crystallinity as there is not much effect shown with the incorporation of glass fiber.

The melting temperature, T_m is mainly related to the degree of hydrogen bonding between the chains, which depends on the density of the amide groups. Thus, as the length of aliphatic groups between the amide link increases, the T_m will drop rapidly, for instance polyamide 6,6 melts at 260ºC compared to polyamide 6,12 at 212ºC [9].

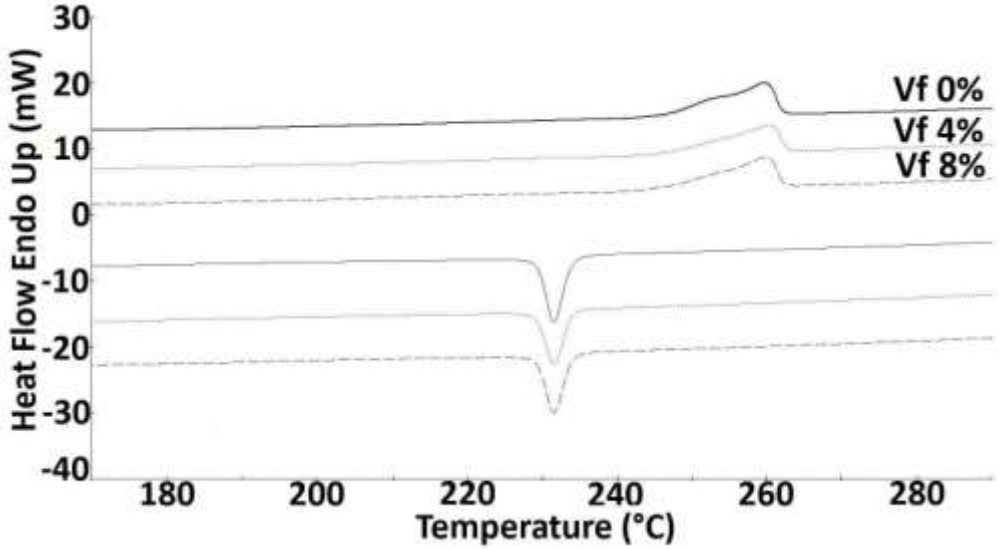

Figure 3: DSC thermograms of injection-molded short glass fiber composites under dry condition

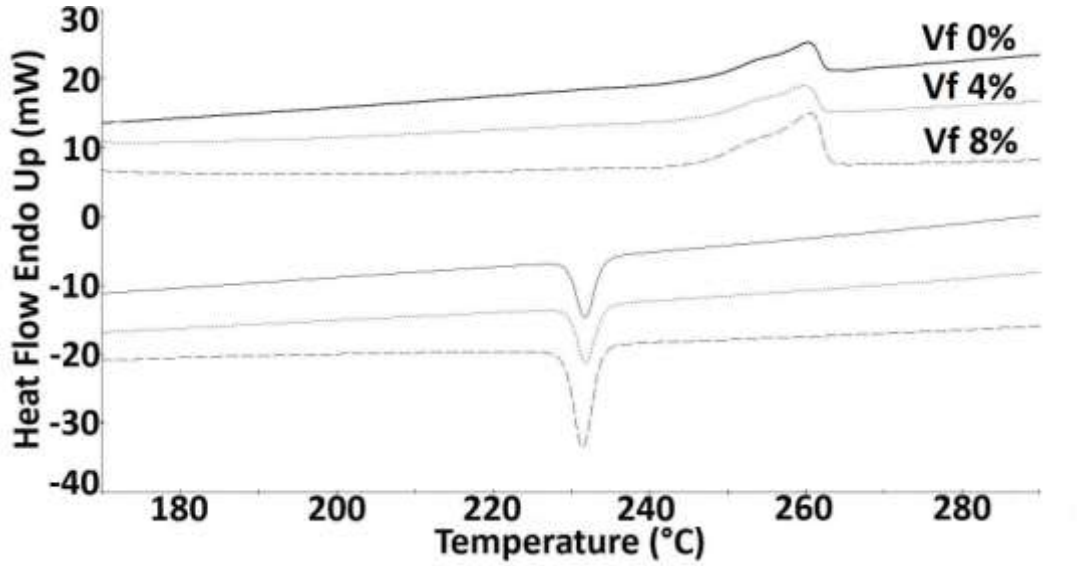

Figure 4: DSC thermograms of injection-molded short glass fiber composites under wet condition

The heating scans show the presence of two melting peaks (Figures 3 and 4). The melting peak at/around 260ºC could be attributed to the melting of the α-crystalline portion of matrix (T_m^{α}). The one at/around 253ºC, (T_m^{γ}) probably indicates the melting of the thermodynamically unstable γ-crystalline [10],[11],[12]. Referring to Figures 3-4, it can be seen that the presence of glass fiber did not produce any apparent effect on the melting temperature of the composites for both conditions. This suggests that the incorporation of glass fiber into the composites does not affect the degree of hydrogen bonding between the polymer chains. As for the crystalline peak temperature, T_c, no significant changes in T_c values are observed with the incorporation of glass fiber and moisture into the system.

3.3 Dynamic Mechanical Properties

Results from dynamic mechanical analyses of the injection molded composites are given in Figures 5 and 6, depicting tan δ against temperature curves. From Figure 5, over a temperature range of –100ºC to 150ºC, two transition regions as indicated by two damping maxima, are recorded for the dry specimens. These transitions are usually known as ß-transition at a lower temperature and α-transition at a higher temperature. The peak which is at maximum value of tan δ in α-transition, T_α is generally known as the glass transition temperature, T_g, while $T_ß$ is referred to temperature at the maximum value of tan δ in ß-transition. $W_{\sqrt{2}}$ is the width of the transition region ($T_e - T_i$) at tan $\delta_{max}/\sqrt{2}$ height. T_e and T_i are respectively the end and initial temperatures of the transition region. For wet specimens (Figure 6), only one transition, T_α is recorded at much lower temperatures compared to the dry specimens. $T_ß$ is eliminated or reduced to below –100ºC and not detected under the present test temperature range.

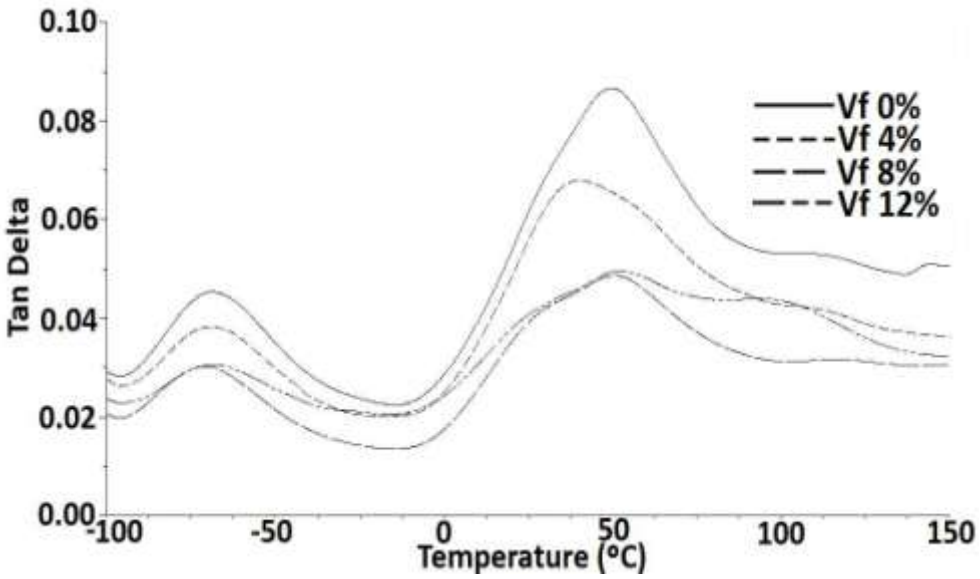

Figure 5: DMA tan delta–temperature behavior of injection-molded short glass fiber composites under dry condition

As shown in Figure 5, the incorporation of fibers produces no significant trend in displacement of the α-relaxation peak for the dry specimens. Composite with 4% V_f of glass fiber shows the lowest T_g (40ºC), compared to the other compositions (50ºC and 52ºC for V_f of 8% and 12% respectively). It is suggested that the incorporation of lower fraction of glass fiber may only give notching effect to the composite. They may introduce a micro void in the composites and instead of reinforcing the matrix, it weakens the composites. There is no change in T_g of composite at V_f of 8% and only a negligible increase of 2ºC at V_f of 12%. On the other hand, the presence of the glass fiber reduces the magnitude of tan δ_{max} values dramatically. Higher reduction for composites with higher fiber loadings is believed due to the strengthening effect by the fibers. Tan δ_{max} of reinforced composites shows a maximum decrease of about 44% compared to the pure matrix (0.0868 to 0.0488). In this instance, the incorporation of fibers acts as barriers to the mobility of polymer chain, leading to lower degree of molecular motion and hence lower damping characteristics [13]. Another possible reason is that there is less matrix by volume to dissipate the vibration energy.

For the effect of V_f on wet specimens, the same trend as for the dry specimens is observed in terms of stability in T_g values and reduction in tan δ_{max}. T_g of all composite specimens recorded a 3ºC decrease compared to the pure matrix (–13ºC to -16^oC). This is believed due to the existence of moisture that weakens the polymer matrix. By chance, tan δ_{max} of reinforced composites show a maximum decrease of also 44% compared to the pure matrix (0.1142 to 0.0637); same magnitude of change as that observed for the dry specimens.

Water uptake decreases the T_g of pure matrix drastically compared to the dry specimens, from 50ºC to –13ºC (reduction of 63ºC). For composite specimens, T_g values reduce from between 40ºC and 52ºC to –16ºC, with a magnitude of between 56ºC to 68ºC. Water uptake also increases the values of tan δ_{max}. For pure matrix, the increase in tan δ_{max} is 32%, from 0.0868 to 0.1142. For composite specimens, the increases are 28% to 51%. From these figures, it can be concluded that the major contributing factor that leads to the reduction in T_g and increase in tan δ_{max} is the moisture uptake, not the fiber loadings.

As can be seen in Figures 5 and 6, tan δ_{max} decrease with the increase in fiber loadings for both dry and wet specimens. This decreases the tan $\delta_{max}/\sqrt{2}$ height, decreases the T_i and increases the T_e and eventually increases the width of **α**-transition region ($W_{\sqrt{2}}$). For the dry specimens, dramatic increase in $W_{\sqrt{2}}$ is shown by samples at all fiber loadings, whereby V_f of 4%, 8% and 12% recorded an increase of $W_{\sqrt{2}}$ by 22%, 29% and 129% compared to the pure matrix (from 49ºC to 60ºC, 63ºC and 112ºC respectively). However, for the wet specimens, there are negligible differences in their T_i, T_e and $W_{\sqrt{2}}$. Composites with V_f of 4%, 8% and 12% recorded an increase of $W_{\sqrt{2}}$ by only 3%, 11% and 8% respectively compared to the pure matrix (from 36ºC to 37ºC, 40ºC and 39ºC respectively). These trends indicate that, under dry condition, glass fiber is a major controlling factor in damping properties. In contrary, under wet condition, fiber becomes less important and matrix is the controlling factor.

Comparing Figures 5 and 6, it can be seen that the tan δ peaks of α-transition for both unreinforced and reinforced PA 6,6 shift to lower values when exposed to humid environment. Since humidity acts as a plasticizer, this induces a further increase in the amorphous chain mobility in the material and hence reduces T_g significantly [14].

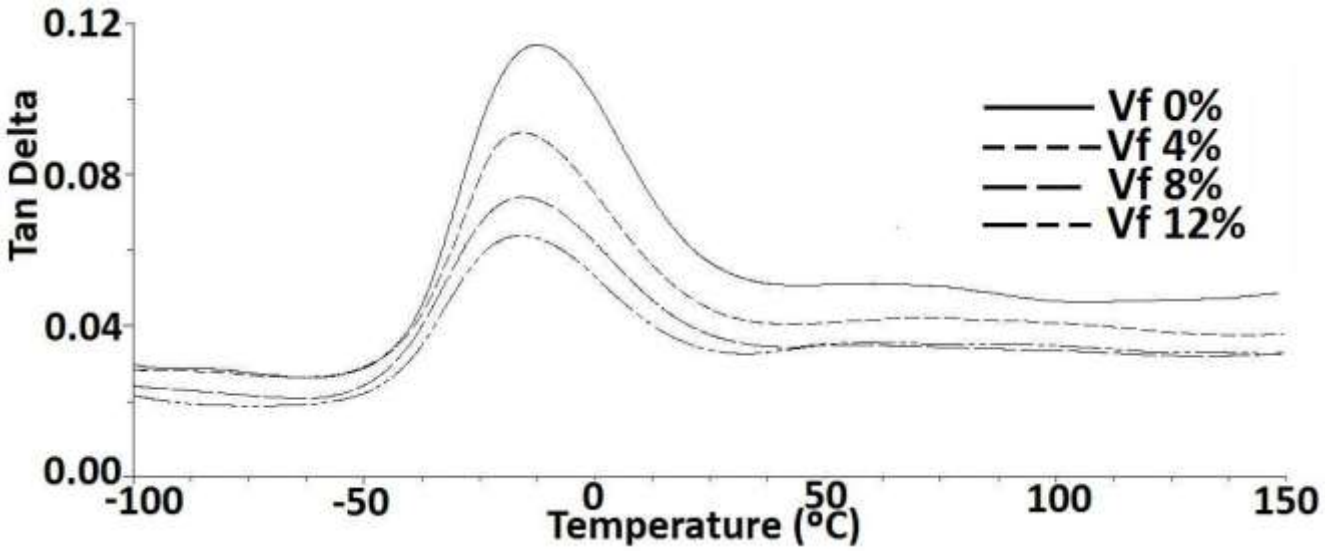

Figure 6: DMA tan delta–temperature behavior of injection-molded short glass fiber composites under wet condition

4. CONCLUSIONS

The glass fiber loading in PA 6,6 produced positive effects on the thermal stability of the composites. The degree of crystallinity of polymer is reduced with incorporation of glass fiber. The introduction of glass fiber and moisture into the composites does not affect the T_m and T_c. The T_g values are not significantly altered by the incorporation of glass fiber into the system. However, its value is reduced with moisture content. The tan δ_{max} decreases with an increase in fiber loadings for both dry and wet specimens.

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